

PATENT ABSTRACTS OF JAPAN

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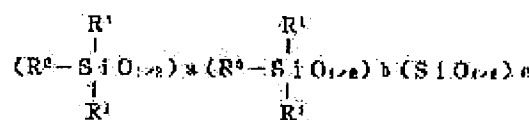
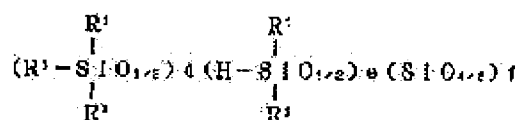
(54) CURABLE SILICONE COMPOSITION

(57)Abstract:

PURPOSE: To obtain a curable silicone composition, consisting essentially of an organopolysiloxane composed of an epoxy group-containing monofunctional siloxane unit and a tetrafunctional siloxane unit and excellent in curability and flexibility and heat resistance or cured products.

CONSTITUTION: The objective curable composition is composed of (A) an organopolysiloxane prepared by carrying out the addition reaction of an organopolysiloxane expressed by formula I [R¹ is monovalent hydrocarbon group except alkenyl group; (d) is 0 or an integer; (e) and (f) are positive numbers; [(d)/(f)] is 0-4; [(e)/(f)] is 0.05-4; [(d)+(e)/(f)] is 0.2-4] with an optional amount of an alkoxysilylalkene and expressed

by formula II [R² is R¹ or H; R³ is epoxy group-containing organic group or alkoxysilylalkyl and at least one thereof is epoxy group-containing organic group; (a) is 0 or a positive number; (b) and (c) are positive numbers; [(a)/(c)] is 0-4; [(b)/(c)] is 0.05-4; [(a)+(b)/(c)] is 0.2-4] and (B) a curing agent and/or a curing catalyst.



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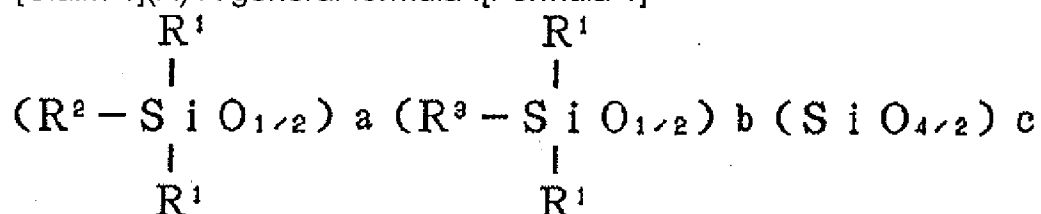
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CLAIMS

[Claim(s)]

[Claim 1](A) A general formula :[Formula 1]



{R¹ is a monovalent hydrocarbon group except an alkenyl group among a formula, and R² is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R³ is an epoxy group content organic group or an alkoxy silyl alkyl group, and at least one in R³ is an epoxy group content organic group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. The hardenability silicone composition which consists of the organopolysiloxane expressed with} and a (B) hardening agent, or a curing catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention about a hardenability silicone composition in detail, It excels in the hardenability which becomes considering the organopolysiloxane which consists of monofunctional siloxane units (M unit) which have an epoxy group content organic group, and tetrafunctional siloxane units (Q unit) as a principal member, and after hardening is related with the hardenability silicone composition used as the silicone hardened material excellent in pliability and heat resistance.

[0002]

[Description of the Prior Art] Since the silicone hardened material after hardening is excellent in an adhesive property, adhesion, weatherability, and an electrical property, the hardenability silicone composition is used for the electrical and electric equipment and the bulking agent for electrons, the electrical and electric equipment and the adhesives for electrons, the paint, the coating material for rubbers, etc. As a hardenability silicone composition, for example, By the dehydrating condensation reaction of silanol groups, the dehydrogenation of a silanol group and a silicon atom absorbed water matter atom, or the dealcoholization reaction of a silanol group and a silicon atom joint alkoxy group. The addition reaction mold-curing nature silicone composition hardened by the addition reaction of a silicon atom hydrogen atom and an aliphatic unsaturated group under existence of the condensation reaction mold-curing nature silicone composition and the catalyst for a hydrosilylation reaction to harden is known.

[0003] However, a condensation reaction mold-curing nature silicone composition, Under existence of addition reaction inhibition nature substances, such as sulfur and solder flux, there was a problem that cure time was very long and hardenability was bad, and hardening did not advance, and the addition reaction mold-curing nature silicone composition had the problem of being hard to harden the surface of this constituent by oxygen. Generally there was a problem

that a hardenability silicone composition had the low heat resistance of the silicone hardened material after hardening.

[0004]For this reason, various hardenability silicone compositions excellent in hardenability are proposed, and as such a hardenability silicone composition, The hardenability silicone composition which consists of the hydrolyzate and ammonium perchlorate of epoxy group content organicity Silang (refer to JP,56-72054,A), And the hardenability silicone composition (refer to JP,60-178417,A) which consists of the organopolysiloxane which contains at least two epoxy groups in one molecule, organopolysiloxane which contains at least two amino groups in one molecule, and an epoxy curing catalyst is proposed.

[0005]

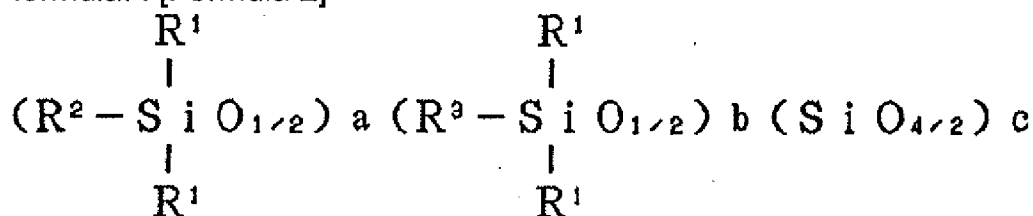
[Problem(s) to be Solved by the Invention]However, the hardenability of the hardenability silicone composition proposed by JP,56-72054,A and JP,60-178417,A cannot be satisfied enough, and there was a problem that the pliability of the silicone hardened material after hardening and heat resistance were inferior and.

[0006]this invention person reached this invention, as a result of inquiring wholeheartedly, in order to solve the above-mentioned problem.

[0007]That is, the purpose of this invention is excellent in hardenability, and there is after hardening in providing the hardenability silicone composition used as the silicone hardened material excellent in pliability and heat resistance.

[0008]

[The method of solving a technical problem, and its operation] This invention is the (A) general formula. : [Formula 2]

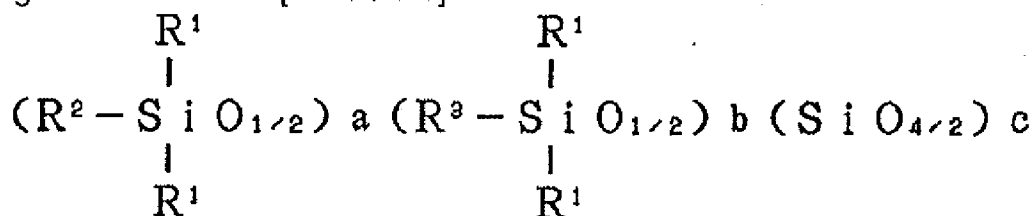


{R¹ is a monovalent hydrocarbon group except an alkenyl group among a formula, and R² is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R³ is an epoxy group content organic group or an alkoxy silyl alkyl group, and at least one in R³ is an epoxy group content organic group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. It is related with the hardenability silicone composition which consists of the organopolysiloxane expressed with} and a (B) hardening agent, or a curing catalyst.

[0009]Hereafter, the hardenability silicone composition of this invention is explained in detail.

[0010](A) Organopolysiloxane of an ingredient is a principal member of this invention, and is a

general formula. : [Formula 3]



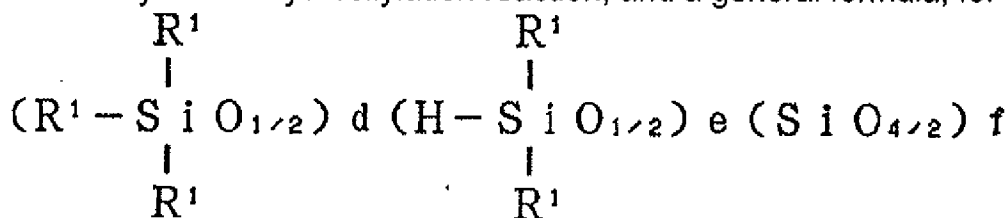
It is come out and expressed. R^1 is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aralkyl groups, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group, a tolyl group, and a xylyl group, and a phenethyl group; substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, etc. are illustrated. R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, and specifically, A hydrogen atom. Or aralkyl groups, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group, a tolyl group, and a xylyl group, and a phenethyl group; substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, etc. are illustrated. R^3 is an epoxy group content organic group or an alkoxy silyl alkyl group, and at least one in R^3 is an epoxy group content organic group. As an epoxy group content organic group, specifically, A glycidoxy ethyl group, a glycidoxy propyl group, A glycidoxybutyl group, a 3,4-epoxycyclohexyl ethyl group, a 3,4-epoxycyclohexyl propyl group, a 3,4-epoxy NORUBORUNE nil ethyl group, a 2-(3,4-epoxy-3-methylcyclohexyl)-2-methylethyl group, etc. are illustrated, As an alkoxy silyl alkyl group for giving an adhesive property to the constituent of this invention, specifically, A trimethoxysilyl ethyl group, a trimethoxysilylpropyl group, a trimethoxysilyl butyl group, a triethoxy silyl ethyl group, a triethoxy silyl propyl group, tripropoxy silylethylene, a methyl dimethoxy silyl ethyl group, A methyl dimethoxy silyl propyl group etc. are illustrated.

[0011]a is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which do not have an epoxy group content organic group or an alkoxy silyl alkyl group among an upper type, b is a positive number which shows the number of the monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and a/c are the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. Monofunctional siloxane units (M unit) cannot have this [good] for four pieces to one tetrafunctional siloxane units (Q unit), In order for the silicone hardened material after hardening to be excellent in pliability and heat resistance, It is because the monofunctional siloxane units (M unit) which have an epoxy group content organic group

or an alkoxy silyl alkyl group need to be at least 0.05 piece to one tetrafunctional siloxane units (Q unit).

[0012](A) Although organopolysiloxane of an ingredient is liquefied at a room temperature, or it is a solid state and the molecular weight in particular is not limited, since hardenability is excellent, it is preferred that it is the range of 500-500,000.

[0013]Organopolysiloxane of the above-mentioned (A) ingredient is the bottom of existence of the catalyst for a hydrosilylation reaction, and a general formula, for example. : [Formula 4]



{R¹ is a monovalent hydrocarbon group except an alkenyl group among a formula. d is 0 or a positive number, e is a positive number, f is a positive number, d/f is the number of 0-4, and e/f is the number of 0.05-4, and (d+e)/f is the number of 0.2-4. It can obtain by carrying out the addition reaction of organopolysiloxane and epoxy group content aliphatic unsaturated hydrocarbon which are expressed with}, and the alkoxy silylalkene of an arbitrary dose.

[0014](B) The hardening agent or curing catalyst of an ingredient is an ingredient for stiffening organopolysiloxane of the (A) ingredient, and especially if it is the hardening agent or curing catalyst which generally stiffens an epoxy resin as a (B) ingredient, it will not be limited. As a hardening agent, they are illustrated by a phenolic compound, a carboxylic acid compound, an acid anhydride, an amine compound, alkoxy group content compounds or these mixtures, and the partial reactant, and specifically as a curing catalyst, Specifically, zirconium compounds, such as aluminum compounds, such as phosphorus compounds, such as tertiary amine compounds, such as imidazole, the 4th class amine compound, and phosphine, and organic aluminum, and an organic zirconium, etc. are illustrated. In the constituent of this invention, either one of a hardening agent or a curing catalyst a hardening agent, and a curing catalyst can be used together and used.

[0015](B) Although the loadings in particular of an ingredient are not limited, it is preferred that it is 0.1 - 500 weight section to (A) ingredient 100 weight section. The loadings of the (B) ingredient are for a hardening reaction to become difficult to occur by less than 0.1 weight sections to (A) ingredient 100 weight section, and this is for a hardening reaction to become fully difficult to occur, even if it exceeds 500 weight sections.

[0016]Although the hardenability silicone composition of this invention consists of the above-mentioned (A) ingredient and a (B) ingredient, As other ingredients, bulking agents, such as haze-like silica, crystalline silica, pyrogenic silica, wet process silica, titanium oxide, zinc carbonate, calcium carbonate, iron oxide, and carbon black, Higher-fatty-acid ester, such as

stearic acid ester and pulmitic acid ester, or metal salt, an ester system wax, or a plasticizer can be blended.

[0017] Since the hardenability silicone composition of this invention is excellent in hardenability and after hardening serves as a silicone hardened material excellent in pliability and heat resistance, It can be conveniently used as sealing compounds of the hot section circumference, such as a coating agent of a paint, and an electron and an electrical part, adhesives, encapsulant for electric electronic components, and an automobile engine, and also a flexible grant agent of a hardenability resin composition.

[0018]

[Example] Hereafter, an example explains this invention. The value of viscosity is a value measured in 25 °C among an example, and at 150 °C, the hardenability silicone composition was heated for 3 hours, and was stiffened. Measurement of the physical property of a silicone hardened material was performed as follows.

O Heat resistance : by thermogravimetric analysis (TGA), temperature up of the wafer of a silicone hardened material was carried out by a part for heating-rate/of 10 °C under air, and it was shown with the survival rate (% of the weight) in 850 °C.

O Pliability : the curvature of the central part was measured, having fixed the both ends of 1/4inchx1 / fabricated cylindrical silicone hardened material (2 inches x 4 inches), and having, applied 5 kg of load subsequently to the central part of a silicone hardened material. The case where the curvature was less than 0.5 cm was made into x, the case where it was 0.5-1 cm was made into **, and the case where it exceeded 1 cm was expressed as O.

O Hardness: The silicone hardened material fabricated to phix1 / 10-inch disk 2 inches was measured with bar call 935 hardness scale.

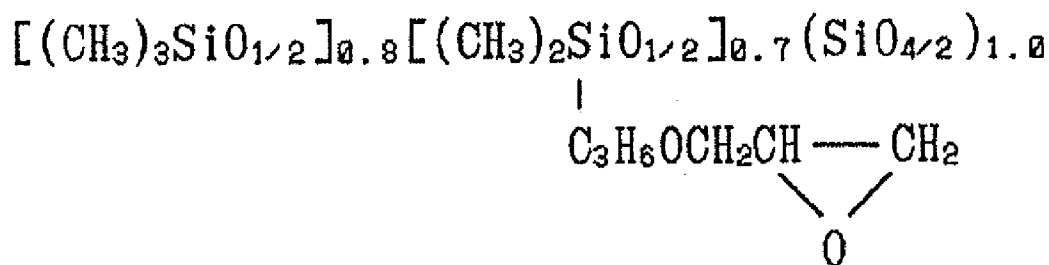
[0019]

[Reference example 1] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/3}\text{SiO}_{3/[(\text{CH}_3)_2]^{0.8}}$

$[(\text{CH}_3)_2]^{0.7}(\text{SiO}_{4/2})^{1.0}$ (105 centipoise viscosity) The organopolysiloxane (A) which makes

chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in 0.40 % of the weight of content of a silicon atom absorbed water matter atom was obtained. The viscosity of this organopolysiloxane was 520 centipoises and the weight per epoxy equivalent was 420.

[Formula 5]

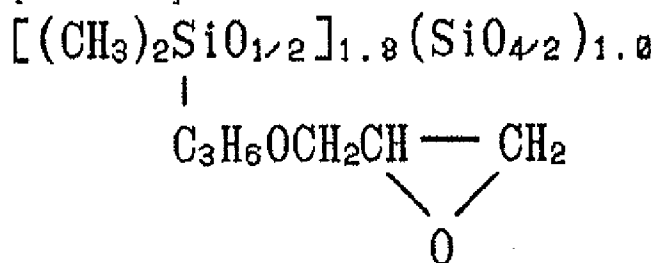


[0020]

[Reference example 2] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/2}/[(\text{CH}_3)_2]_{1.8}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) The organopolysiloxane (B) which makes chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in 0.92 % of the weight of content of a silicon atom absorbed water matter atom was obtained. The viscosity of this organopolysiloxane was 610 centipoises and the weight per epoxy equivalent was 370.

[Formula 6]

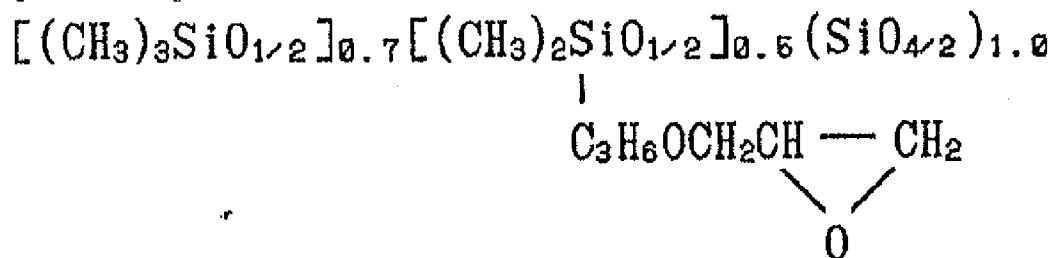


[0021]

[Reference example 3] Formula : The consistency organopolysiloxane (0.33 % of the weight of content of a silicon atom absorbed water matter atom) expressed with $2\text{HSiO}_{1/2}/3\text{SiO}_{3/2}/[(\text{CH}_3)_2]_{1.8}$

$0.7[(\text{CH}_3)_2]_{0.5}(\text{SiO}_{4/2})_{1.0}$ in toluene, The organopolysiloxane (C) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. this organopolysiloxane -- brown -- it was translucent and the weight per epoxy equivalent was 1100.

[Formula 7]

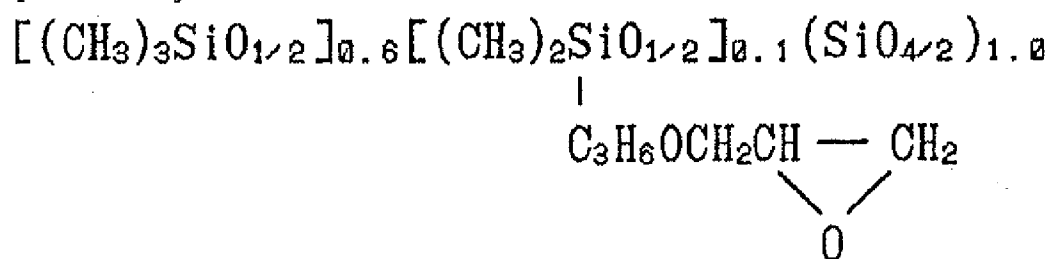


[0022]

[Reference example 4] Formula : The organopolysiloxane (0.09 % of the weight of content of a silicon atom absorbed water matter atom) expressed with $2\text{HSiO}_{1/3}\text{SiO}_{3/2}[(\text{CH}_3)_2]_{0.6}[(\text{CH}_3)_2]_{0.1}$

$(\text{SiO}_{4/2})_{1.0}$ in toluene, The organopolysiloxane (D) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. This organopolysiloxane was brown transparence and the weight per epoxy equivalent was 1290.

[Formula 8]

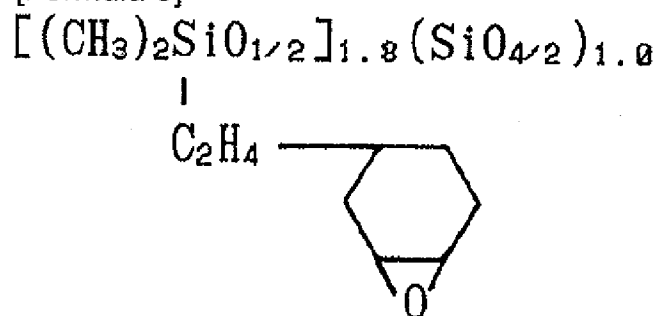


[0023]

[Reference example 5] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/2}[(\text{CH}_3)_2]_{1.8}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) The organopolysiloxane (E) which makes chloroplatinic acid react as a catalyst and is shown [cyclosiloxane / superfluous in toluene / 1,2-epoxy-4-vinyl] by a lower formula in 0.92 % of the weight of content of a silicon atom absorbed water matter atom was obtained. This organopolysiloxane was brown transparence, that viscosity was 520 centipoises, and the weight per epoxy equivalent was 230.

[Formula 9]



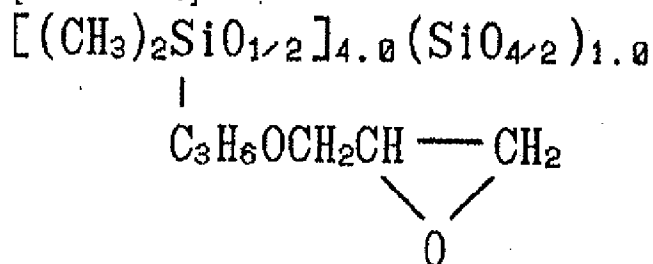
[0024]

[Reference example 6] Formula : The organopolysiloxane (1.22 % of the weight of content of 190 ** of boiling points, and a silicon atom absorbed water matter atom) expressed with $2\text{HSiO}_{1/2}[(\text{CH}_3)_2]_{4.0}(\text{SiO}_{4/2})_{1.0}$ in toluene, The organopolysiloxane (F) which makes

chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. This organopolysiloxane was brown transparence, that viscosity

was 54 centipoises, and the weight per epoxy equivalent was 205.

[Formula 10]

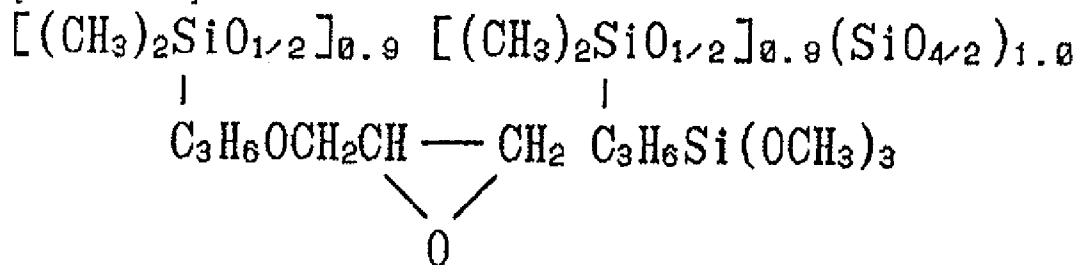


[0025]

[Reference example 7] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/2}[(\text{CH}_3)_2]_{1.8}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) 0.92 % of the weight of content of a silicon atom absorbed water matter atom in toluene, The organopolysiloxane (G) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in the mixture which consists of allyl glycidyl ether and allyl trimethoxysilane =1:1 was obtained to the silicon atom absorbed water matter atom in organopolysiloxane. This organopolysiloxane was yellow transparence and that viscosity was 200 centipoises.

[Formula 11]



[0026]

[Work example 1] Organopolysiloxane, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate which were prepared by the reference example, 3 or 4-methylhexa HAIDOROFUTARIKKU anhydride, and 2,4,6-(tris dimethylamino methyl) phenol were uniformly mixed with the number of weight sections shown in Table 1, and the hardenability silicone composition was prepared. These hardenability silicone compositions were stiffened and the physical property of the obtained silicone hardened material was measured. These results were shown in Table 1. The hardness after hardening of the hardenability silicone composition which blends the organopolysiloxane B prepared by the reference example 2 was 55.

[0027]

[Comparative example 1] Except for organopolysiloxane, the hardenability epoxy resin composition was prepared with the number of weight sections shown in Table 1 for

comparison. This hardenability epoxy resin composition was stiffened like Example 1, and the physical property of the obtained hardened material was measured. This result was shown in Table 1. The hardness of this hardened material is 55 and it was checked that there are no hardness and difference of the silicone hardened material measured in Example 1.

[0028]

[Table 1]

	本 発 明						比較例
	A	B	C/F	D/G	E	E	
オルガノポリシリキサンの種類							—
オルガノポリシリキサン	100	100	95/5	95/5	100	50	—
3,4-エポキシジクロロヘキシルメチル-3,4-エポキシジクロロヘキサンカルボキシレート	—	—	—	—	—	50	100
3または4-メチルヘキサハイドロ7タリツクアソルイトライト	37.6	42.7	14.4	12.2	40.5	76.6	120.5
2,4,6-(トリシジメチルアミノメチル)フェノール	1	1	1	1	1	1	1
柔軟性	○	○	○	△	△	△	×
残存率 (重量%)	33	25	55	63	27	11	0

[0029]

[Work example 2] In Example 1, the hardenability silicone composition was prepared like Example 1 except having added fused silica with a mean particle diameter of 13 micrometers.

The obtained hardenability silicone composition was stiffened like Example 1, and the physical property of the obtained silicone hardened material was measured. This result was shown in Table 2.

[0030]

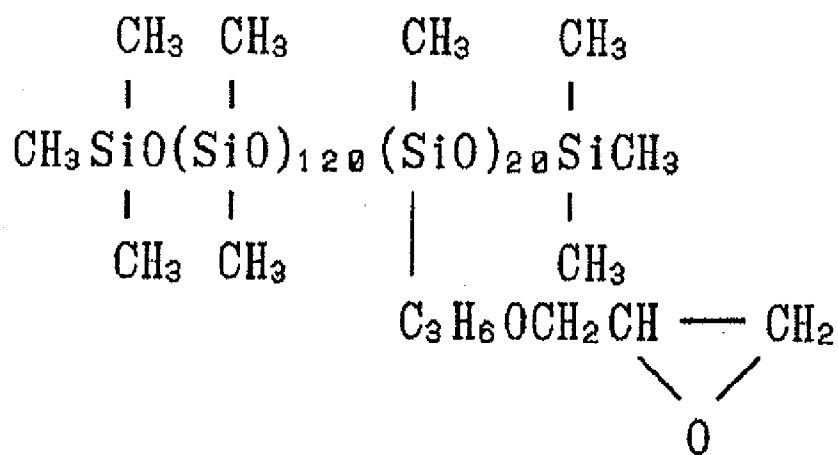
[Table 2]

	本 発 明	
オルガノポリシロキサンの種類	E	E
オルガノポリシロキサン	100	50
3,4-エポキシシクロヘキシルメチル-3,4-エポキシシクロヘキサンカルボキシレート	—	50
3または4-メチルヘキサハイドロフタリック アンハイドライド	40.5	76.6
熔融シリカ	137.5	169.9
2,4,6-(トリメチルアミノメチル)フェノール	1	1
柔軟性	△	△
残存率 (重量%)	65	57

[0031]

[Comparative example 2] The hardenability silicone composition was prepared like Example 1 except having used the organopolysiloxane shown in the lower type. Since organopolysiloxane of the lower type separated into the surface on the way of [hardening], this hardenability silicone composition was not able to evaluate the physical property of the hardened material.

[Formula 12]



[0032]

[Effect of the Invention]The hardenability silicone composition of this invention consists of a (A) ingredient and a (B) ingredient, Especially, since the (A) ingredient is organopolysiloxane which consists of monofunctional siloxane units (M unit) which have an epoxy group content organic group, and tetrafunctional siloxane units (Q unit), it excels in hardenability and after hardening has the feature of becoming the silicone hardened material excellent in pliability and heat resistance.

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TECHNICAL FIELD

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PRIOR ART

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, the hardenability of the hardenability silicone composition proposed by JP,56-72054,A and JP,60-178417,A cannot be satisfied enough, and there was a problem that the pliability of the silicone hardened material after hardening and heat resistance were inferior and.

[0006]this invention person reached this invention, as a result of inquiring wholeheartedly, in order to solve the above-mentioned problem.

[0007]That is, the purpose of this invention is excellent in hardenability, and there is after hardening in providing the hardenability silicone composition used as the silicone hardened material excellent in pliability and heat resistance.

[Translation done.]

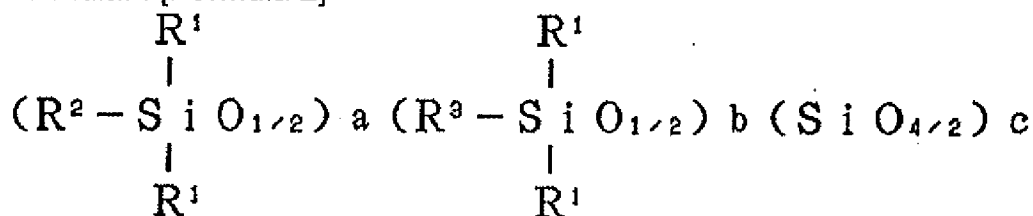
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OPERATION

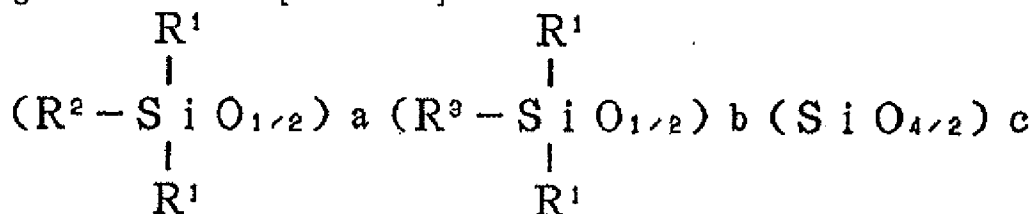
[A method of solving a technical problem, and its operation] This invention is the (A) general formula. : [Formula 2]



{R¹ is a monovalent hydrocarbon group except an alkenyl group among a formula, and R² is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, R³ is an epoxy group content organic group or an alkoxy silyl alkyl group, and at least one in R³ is an epoxy group content organic group. a is 0 or a positive number, b is a positive number, c is a positive number, a/c is the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. It is related with the hardenability silicone composition which consists of the organopolysiloxane expressed with} and a (B) hardening agent, or a curing catalyst.

[0009] Hereafter, the hardenability silicone composition of this invention is explained in detail.

[0010] (A) Organopolysiloxane of an ingredient is a principal member of this invention, and is a general formula. : [Formula 3]



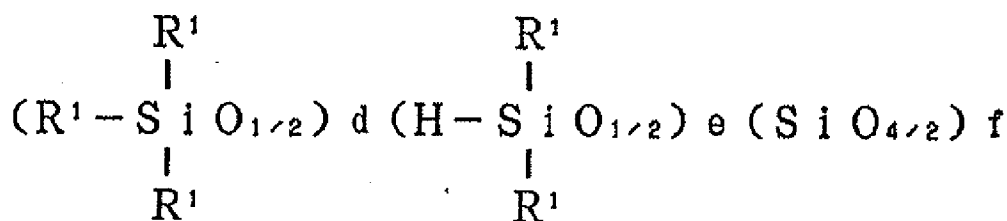
It is come out and expressed. R¹ is a monovalent hydrocarbon group except an alkenyl group among an upper type, and specifically, Aralkyl groups, such as aryl group; benzyls, such as

alkyl group; phenyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group, a tolyl group, and a xylyl group, and a phenethyl group; substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, etc. are illustrated. R^2 is the monovalent hydrocarbon group or hydrogen atom except an alkenyl group, and specifically, A hydrogen atom. Or aralkyl groups, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group, a tolyl group, and a xylyl group, and a phenethyl group; substituted alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, etc. are illustrated. R^3 is an epoxy group content organic group or an alkoxy silyl alkyl group, and at least one in R^3 is an epoxy group content organic group. As an epoxy group content organic group, specifically, A glycidoxy ethyl group, a glycidoxy propyl group, A glycidoxybutyl group, a 3,4-epoxycyclohexyl ethyl group, a 3,4-epoxycyclohexyl propyl group, a 3,4-epoxy NORUBORUNE nil ethyl group, a 2-(3,4-epoxy-3-methylcyclohexyl)-2-methylethyl group, etc. are illustrated, As an alkoxy silyl alkyl group for giving an adhesive property to the constituent of this invention, specifically, A trimethoxysilyl ethyl group, a trimethoxysilylpropyl group, a trimethoxysilyl butyl group, a triethoxy silyl ethyl group, a triethoxy silyl propyl group, tripropoxy silylethylene, a methyl dimethoxy silyl ethyl group, A methyl dimethoxy silyl propyl group etc. are illustrated.

[0011]a is 0 or the positive number which shows the number of the monofunctional siloxane units (M unit) which do not have an epoxy group content organic group or an alkoxy silyl alkyl group among an upper type, b is a positive number which shows the number of the monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group, c is a positive number which shows the number of tetrafunctional siloxane units (Q unit), each ratio and a/c are the number of 0-4, and b/c is the number of 0.05-4, and (a+b)/c is the number of 0.2-4. Monofunctional siloxane units (M unit) cannot have this [good] for four pieces to one tetrafunctional siloxane units (Q unit), In order for the silicone hardened material after hardening to be excellent in pliability and heat resistance, It is because the monofunctional siloxane units (M unit) which have an epoxy group content organic group or an alkoxy silyl alkyl group need to be at least 0.05 piece to one tetrafunctional siloxane units (Q unit).

[0012](A) Although organopolysiloxane of an ingredient is liquefied at a room temperature, or it is a solid state and the molecular weight in particular is not limited, since hardenability is excellent, it is preferred that it is the range of 500-500,000.

[0013]Organopolysiloxane of the above-mentioned (A) ingredient is the bottom of existence of the catalyst for a hydrosilylation reaction, and a general formula, for example. : [Formula 4]



{R¹ is a monovalent hydrocarbon group except an alkenyl group among a formula. d is 0 or a positive number, e is a positive number, f is a positive number, d/f is the number of 0-4, and e/f is the number of 0.05-4, and (d+e)/f is the number of 0.2-4. It can obtain by carrying out the addition reaction of organopolysiloxane and epoxy group content aliphatic unsaturated hydrocarbon which are expressed with}, and the alkoxy silylalkene of an arbitrary dose.

[0014](B) A hardening agent or a curing catalyst of an ingredient is an ingredient for stiffening organopolysiloxane of the (A) ingredient.

(B) It will not be limited especially if it is a hardening agent or a curing catalyst which generally stiffens an epoxy resin as an ingredient.

As a hardening agent, they are illustrated by a phenolic compound, a carboxylic acid compound, an acid anhydride, an amine compound, alkoxy group content compounds or these mixtures, and partial reactant, and specifically as a curing catalyst, Specifically, zirconium compounds, such as aluminum compounds, such as phosphorus compounds, such as tertiary amine compounds, such as imidazole, the 4th class amine compound, and phosphine, and organic aluminum, and an organic zirconium, etc. are illustrated. In a constituent of this invention, either one of a hardening agent or a curing catalyst a hardening agent, and a curing catalyst can be used together and used.

[0015](B) Although loadings in particular of an ingredient are not limited, it is preferred that it is 0.1 - 500 weight section to (A) ingredient 100 weight section. Loadings of the (B) ingredient of this are for a hardening reaction to become difficult to occur by less than 0.1 weight sections to (A) ingredient 100 weight section.

It is for a hardening reaction to become fully difficult to occur, even if it exceeds 500 weight sections.

[0016]Although a hardenability silicone composition of this invention consists of the above-mentioned (A) ingredient and a (B) ingredient, As other ingredients, bulking agents, such as haze-like silica, crystalline silica, pyrogenic silica, wet process silica, titanium oxide, zinc carbonate, calcium carbonate, iron oxide, and carbon black, Higher-fatty-acid ester, such as stearic acid ester and pulmitic acid ester, or metal salt, an ester system wax, or a plasticizer can be blended.

[0017]Since a hardenability silicone composition of this invention is excellent in hardenability and after hardening serves as a silicone hardened material excellent in pliability and heat

resistance, It can be conveniently used as sealing compounds of the hot section circumference, such as a coating agent of a paint, and an electron and an electrical part, adhesives, encapsulant for electric electronic components, and an automobile engine, and also a flexible grant agent of a hardenability resin composition.

[Translation done.]

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EXAMPLE

[Example] Hereafter, an example explains this invention. The value of viscosity is a value measured in 25 ** among an example, and at 150 **, the hardenability silicone composition was heated for 3 hours, and was stiffened. Measurement of the physical property of a silicone hardened material was performed as follows.

O Heat resistance : by thermogravimetric analysis (TGA), temperature up of the wafer of a silicone hardened material was carried out by a part for heating-rate/of 10 ** under air, and it was shown with the survival rate (% of the weight) in 850 **.

O Pliability : the curvature of the central part was measured, having fixed the both ends of 1/4inchx1 / fabricated cylindrical silicone hardened material (2 inches x 4 inches), and having, applied 5 kg of load subsequently to the central part of a silicone hardened material. The case where the curvature was less than 0.5 cm was made into x, the case where it was 0.5-1 cm was made into **, and the case where it exceeded 1 cm was expressed as O.

O Hardness: The silicone hardened material fabricated to phix1 / 10-inch disk 2 inches was measured with bar call 935 hardness scale.

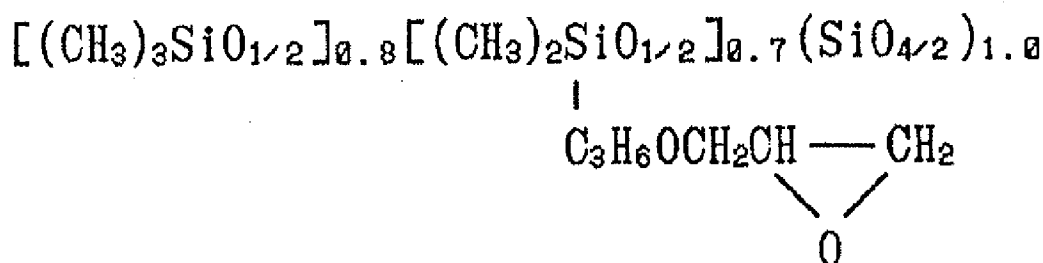
[0019]

[Reference example 1] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/3}\text{SiO}_{3/[(\text{CH}_3)_2]^{0.8}}$

$[(\text{CH}_3)_2]^{0.7}(\text{SiO}_{4/2})^{1.0}$ (105 centipoise viscosity) The organopolysiloxane (A) which makes

chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in 0.40 % of the weight of content of a silicon atom absorbed water matter atom was obtained. The viscosity of this organopolysiloxane was 520 centipoises and the weight per epoxy equivalent was 420.

[Formula 5]

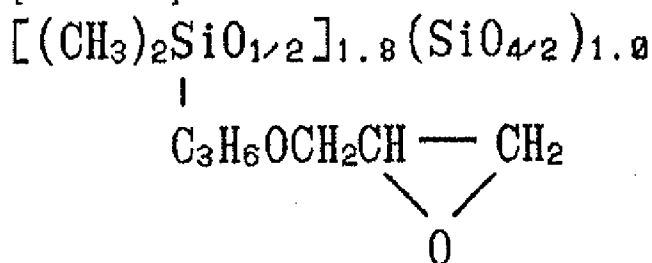


[0020]

[Reference example 2] Formula: Organopolysiloxane expressed with ${}_2\text{HSiO}_{1/3}[(\text{CH}_3)_2]_{1.8}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) The organopolysiloxane (B) which makes chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in 0.92 % of the weight of content of a silicon atom absorbed water matter atom was obtained. The viscosity of this organopolysiloxane was 610 centipoises and the weight per epoxy equivalent was 370.

[Formula 6]

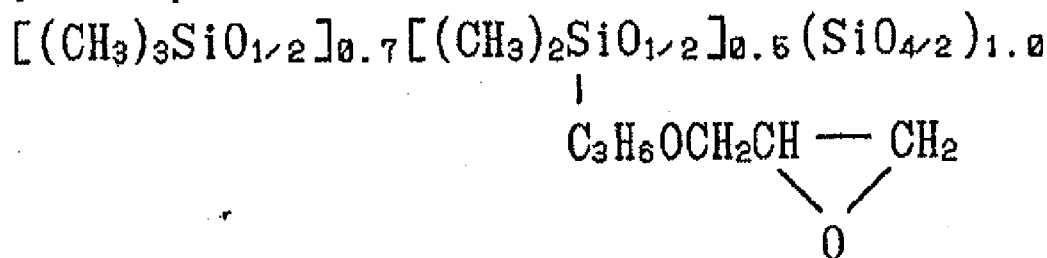


[0021]

[Reference example 3] Formula : The consistency organopolysiloxane (0.33 % of the weight of content of a silicon atom absorbed water matter atom) expressed with ${}_2\text{HSiO}_{1/3}\text{SiO}_{3/3}[(\text{CH}_3)_2]_{0.7}$

$[(\text{CH}_3)_2]_{0.5}(\text{SiO}_{4/2})_{1.0}$ in toluene, The organopolysiloxane (C) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. this organopolysiloxane -- brown -- it was translucent and the weight per epoxy equivalent was 1100.

[Formula 7]

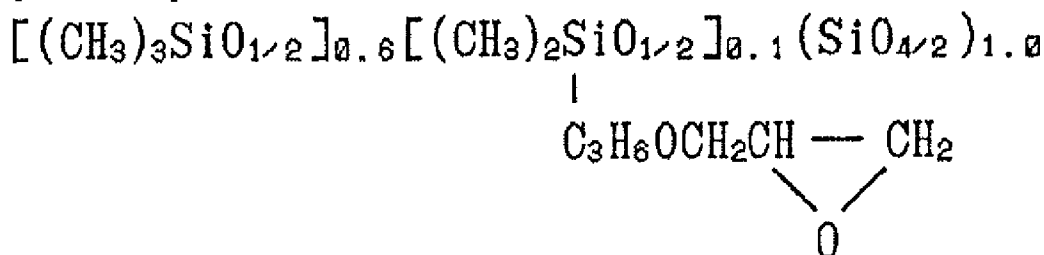


[0022]

[Reference example 4] Formula : The organopolysiloxane (0.09 % of the weight of content of a silicon atom absorbed water matter atom) expressed with $2\text{HSiO}_{1/3}\text{SiO}_{3/[(\text{CH}_3)_2]^{0.6}[(\text{CH}_3)_2]^{0.1}}$

$(\text{SiO}_{4/2})_{1.0}$ in toluene, The organopolysiloxane (D) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. This organopolysiloxane was brown transparence and the weight per epoxy equivalent was 1290.

[Formula 8]

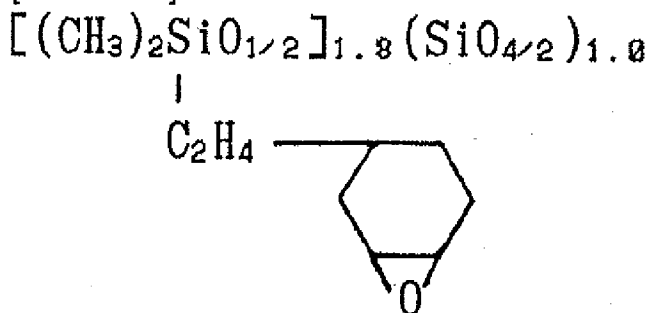


[0023]

[Reference example 5] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/[(\text{CH}_3)_2]^{1.8}}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) The organopolysiloxane (E) which makes chloroplatinic acid react as a catalyst and is shown [cyclosiloxane / superfluous in toluene / 1,2-epoxy-4-vinyl] by a lower formula in 0.92 % of the weight of content of a silicon atom absorbed water matter atom was obtained. This organopolysiloxane was brown transparence, that viscosity was 520 centipoises, and the weight per epoxy equivalent was 230.

[Formula 9]



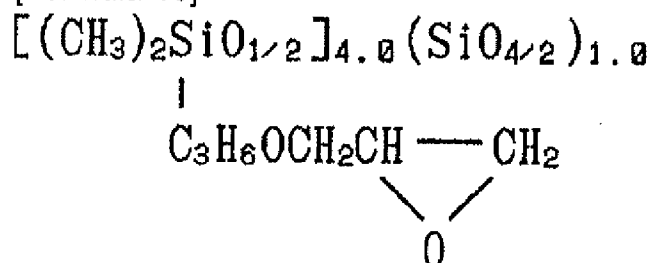
[0024]

[Reference example 6] Formula : The organopolysiloxane (1.22 % of the weight of content of 190 ** of boiling points, and a silicon atom absorbed water matter atom) expressed with $2\text{HSiO}_{1/[(\text{CH}_3)_2]^{4.0}(\text{SiO}_{4/2})_{1.0}}$ in toluene, The organopolysiloxane (F) which makes

chloroplatinic acid react as a catalyst and is shown by a lower formula in superfluous allyl glycidyl ether was obtained. This organopolysiloxane was brown transparence, that viscosity

was 54 centipoises, and the weight per epoxy equivalent was 205.

[Formula 10]

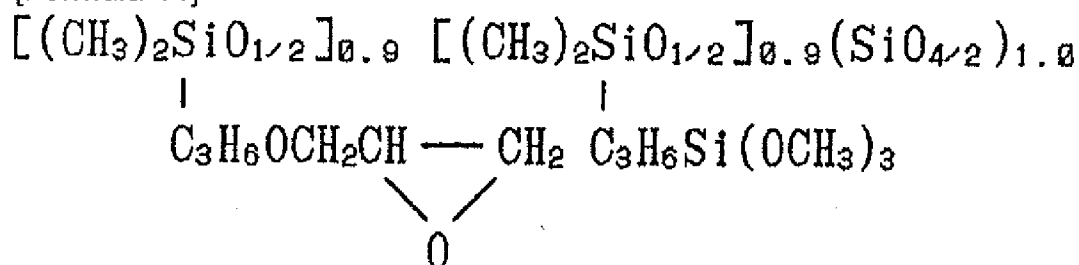


[0025]

[Reference example 7] Formula: Organopolysiloxane expressed with $2\text{HSiO}_{1/2}[(\text{CH}_3)_2]_{1.8}$

$(\text{SiO}_{4/2})_{1.0}$ (46 centipoise viscosity) 0.92 % of the weight of content of a silicon atom absorbed water matter atom in toluene, The organopolysiloxane (G) which makes chloroplatinic acid react as a catalyst and is shown by a lower formula in the mixture which consists of allyl glycidyl ether and allyl trimethoxysilane =1:1 was obtained to the silicon atom absorbed water matter atom in organopolysiloxane. This organopolysiloxane was yellow transparence and that viscosity was 200 centipoises.

[Formula 11]



[0026]

[Work example 1] Organopolysiloxane, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate which were prepared by the reference example, 3 or 4-methylhexa HAIDOROFUTARIKKU anhydride, and 2,4,6-(tris dimethylamino methyl) phenol were uniformly mixed with the number of weight sections shown in Table 1, and the hardenability silicone composition was prepared. These hardenability silicone compositions were stiffened and the physical property of the obtained silicone hardened material was measured. These results were shown in Table 1. The hardness after hardening of the hardenability silicone composition which blends the organopolysiloxane B prepared by the reference example 2 was 55.

[0027]

[Comparative example 1] Except for organopolysiloxane, the hardenability epoxy resin composition was prepared with the number of weight sections shown in Table 1 for

comparison. This hardenability epoxy resin composition was stiffened like Example 1, and the physical property of the obtained hardened material was measured. This result was shown in Table 1. The hardness of this hardened material is 55 and it was checked that there are no hardness and difference of the silicone hardened material measured in Example 1.

[0028]

[Table 1]

	本 発 明						比較例
	A	B	C/F	D/G	E	E	
オルガノシリキサンの種類							—
オルガノシリキサン	100	100	95/5	95/5	100	50	—
3,4-エポキシシリルヘキサメチル-3,4-エポキシシリルヘキサメチルキシレート	—	—	—	—	—	50	100
3または4-メチルヘキサイトロフタリックアノイトライト	37.6	42.7	14.4	12.2	40.5	76.6	120.5
2,4,6-(トリシメチルアミノメチル)フェノール	1	1	1	1	1	1	1
柔軟性	○	○	○	△	△	△	×
残存率 (重量%)	33	25	55	63	27	11	0

[0029]

[Work example 2] In Example 1, the hardenability silicone composition was prepared like Example 1 except having added fused silica with a mean particle diameter of 13 micrometers.

The obtained hardenability silicone composition was stiffened like Example 1, and the physical property of the obtained silicone hardened material was measured. This result was shown in Table 2.

[0030]

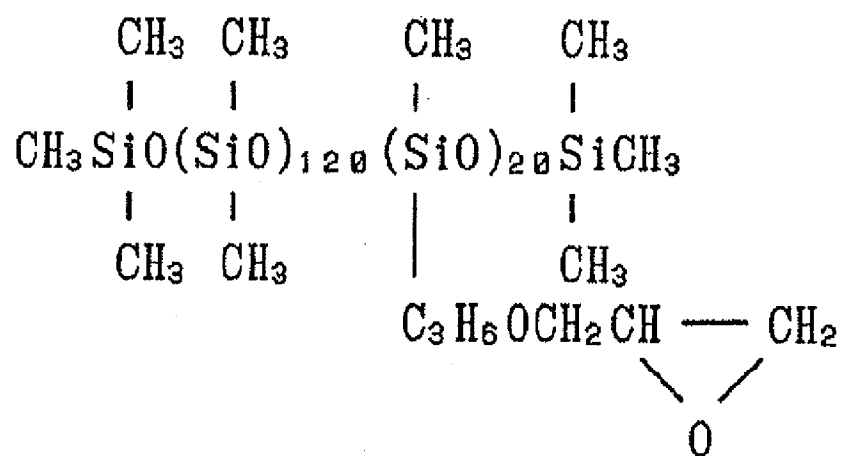
[Table 2]

	本 発 明	
オルカ [*] ノホ [*] リシロキサン [*] の種類	E	E
オルカ [*] ノホ [*] リシロキサン	100	50
3,4-エホ [*] キシシクロヘキシルメチル-3,4-エホ [*] キシシクロヘキサンカルホ [*] キシレート	—	50
3 または 4-メチルヘキサハイト [*] ロフトリック アンハイト [*] ライト [*]	40.5	76.6
溶融シリカ	137.5	139.9
2,4,6-(トリスシ [*] メチルアミノメチル)フェノール	1	1
柔軟性	△	△
残存率 (重量%)	65	57

[0031]

[Comparative example 2] The hardenability silicone composition was prepared like Example 1 except having used the organopolysiloxane shown in the lower type. Since organopolysiloxane of the lower type separated into the surface on the way of [hardening], this hardenability silicone composition was not able to evaluate the physical property of the hardened material.

[Formula 12]



[Translation done.]

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WRITTEN AMENDMENT

----- [Written amendment]

[Filing date]December 10, Heisei 4

[Amendment 1]

[Document to be Amended]Specification

[Item(s) to be Amended]0004

[Method of Amendment]Change

[Proposed Amendment]

[0004]For this reason, various hardenability silicone compositions excellent in hardenability are proposed, and as such a hardenability silicone composition, The hardenability silicone composition which consists of the hydrolyzate and ammonium perchlorate of epoxy group content organicity Silang (refer to JP,56-72054,A), And the hardenability silicone composition (refer to JP,60-179417,A) which consists of the organopolysiloxane which contains at least two epoxy groups in one molecule, organopolysiloxane which contains at least two amino groups in one molecule, and an epoxy curing catalyst is proposed.

[Amendment 2]

[Document to be Amended]Specification

[Item(s) to be Amended]0005

[Method of Amendment]Change

[Proposed Amendment]

[0005]

[Problem(s) to be Solved by the Invention]However, the hardenability of the hardenability silicone composition proposed by JP,56-72054,A and JP,60-179417,A cannot be satisfied enough, and there was a problem that the pliability of the silicone hardened material after hardening and heat resistance were inferior and.

[Written amendment]

[Filing date]March 30, Heisei 5

[Amendment 1]

[Document to be Amended]Specification

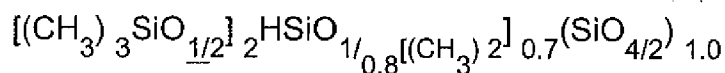
[Item(s) to be Amended]0019

[Method of Amendment]Change

[Proposed Amendment]

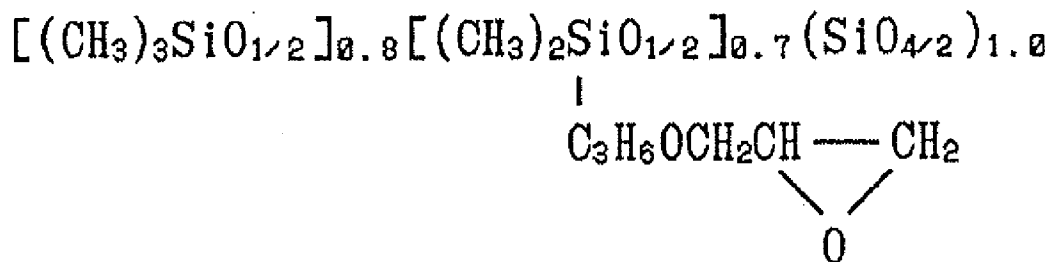
[0019]

[Reference example 1] Formula :



It came out and the organopolysiloxane (A) which makes chloroplatinic acid superfluous ally glycidyl ether react as a catalyst in toluene, and is shown by a lower formula in the organopolysiloxane (0.40 % of the weight of content of 105 centipoise viscosity and a silicon atom absorbed water matter atom) expressed was obtained. The viscosity of this organopolysiloxane was 520 centipoises and the weight per epoxy equivalent was 420.

[Formula 5]



[Amendment 2]

[Document to be Amended]Specification

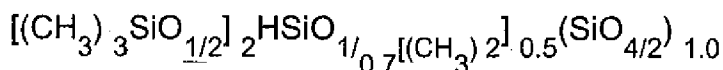
[Item(s) to be Amended]0021

[Method of Amendment]Change

[Proposed Amendment]

[0021]

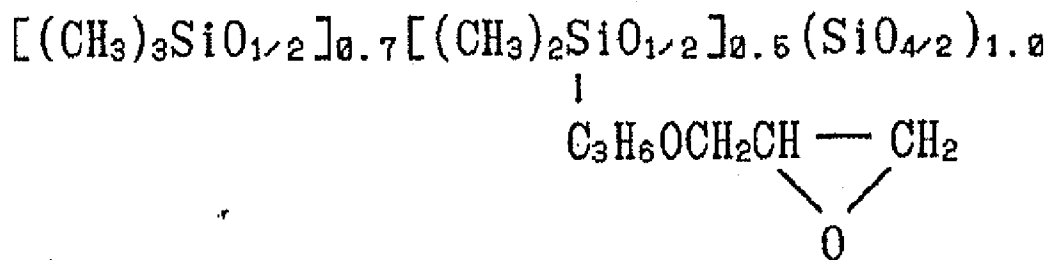
[Reference example 3] Formula :



The organopolysiloxane (C) which comes out, makes chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in the consistency organopolysiloxane (0.33 % of the weight of content of a silicon atom absorbed

water matter atom) expressed was obtained. this organopolysiloxane -- brown -- it was translucent and the weight per epoxy equivalent was 1100.

[Formula 7]



[Amendment 3]

[Document to be Amended] Specification

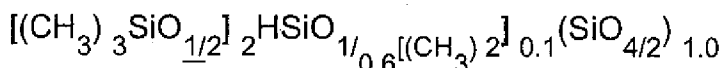
[Item(s) to be Amended] 0022

[Method of Amendment] Change

[Proposed Amendment]

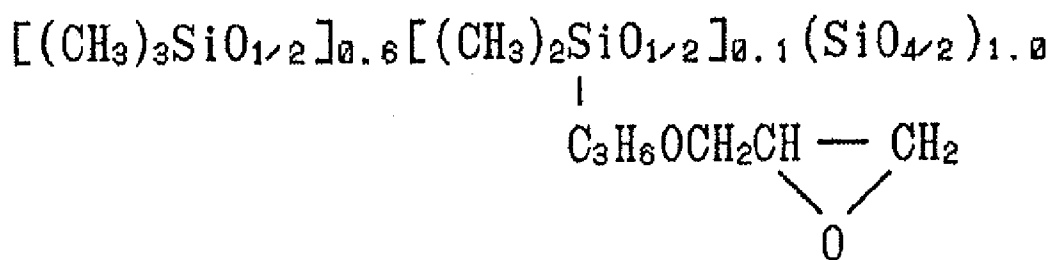
[0022]

[Reference example 4] Formula :



The organopolysiloxane (D) which comes out, makes chloroplatinic acid react as a catalyst and is shown [allyl glycidyl ether / superfluous in toluene] by a lower formula in the organopolysiloxane (0.09 % of the weight of content of a silicon atom absorbed water matter atom) expressed was obtained. This organopolysiloxane was brown transparency and the weight per epoxy equivalent was 1290.

[Formula 8]



[Translation done.]

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(12) 公開特許公報 (A)

(11) 特許出願公開番号

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(71) 出願人 000110077

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コーニング・シリコン株式会社研究開発
本部内

(54) 【発明の名称】 硬化性シリコン組成物

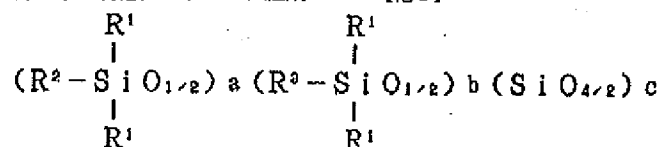
(57) 【要約】

【目的】 硬化性に優れ、硬化後は柔軟性および耐熱性
に優れたシリコン硬化物となる硬化性シリコン組成*

*物を提供する。

【構成】 (A)一般式:

【化1】

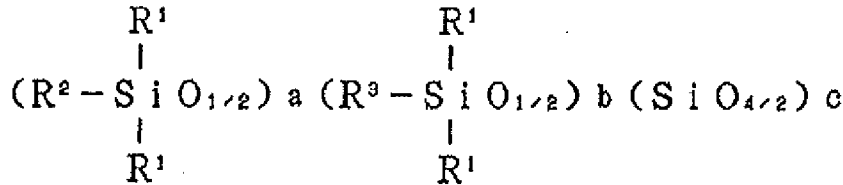


{式中、R¹はアルケニル基を除く一価炭化水素基であり、R²はアルケニル基を除く一価炭化水素基または水素原子であり、R³はエポキシ基含有有機基またはアルコキシシリルアルキル基であり、かつR³の内少なくとも1個はエポキシ基含有有機基である。また、aは0ま

たは正数であり、bは正数であり、cは正数であり、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である}で表されるオルガノポリシロキサン、および(B)硬化剤または硬化触媒からなる硬化性シリコン組成物。

【特許請求の範囲】

【請求項1】 (A)一般式：



【式中、R¹はアルケニル基を除く一価炭化水素基であり、R²はアルケニル基を除く一価炭化水素基または水素原子であり、R³はエポキシ基含有有機基またはアルコキシシリルアルキル基であり、かつR³の内少なくとも1個はエポキシ基含有有機基である。また、aは0または正数であり、bは正数であり、cは正数であり、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。】で表されるオルガノポリシロキサン、および(B)硬化剤または硬化触媒からなる硬化性シリコン組成物。

【発明の詳細な説明】

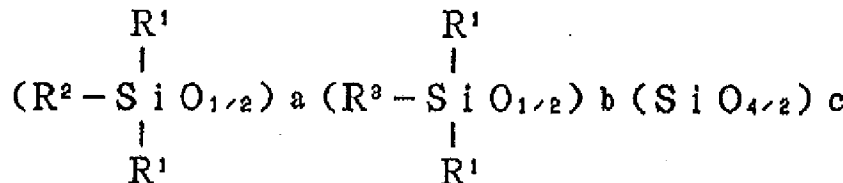
【0001】

【産業上の利用分野】本発明は、硬化性シリコン組成物に関し、詳しくは、エポキシ基含有有機基を有する一官能性シロキサン単位(M単位)と四官能性シロキサン単位(Q単位)とからなるオルガノポリシロキサンを主材としてなる、硬化性に優れ、硬化後は柔軟性および耐熱性に優れたシリコン硬化物となる硬化性シリコン組成物に関する。

【0002】

【従来の技術】硬化性シリコン組成物は、硬化後のシリコン硬化物が接着性、密着性、耐候性、電気特性に優れることから、電気・電子用充填剤、電気・電子用接着剤、塗料、ゴム用コーティング材等に使用されている。硬化性シリコン組成物としては、例えば、シラノール基同士の脱水縮合反応やシラノール基とケイ素原子結合水素原子との脱水素反応またはシラノール基とケイ素原子結合アルコキシ基との脱アルコール反応により硬化する縮合反応型硬化性シリコン組成物やヒドロシリル化反应用触媒の存在下でケイ素原子水素原子と脂肪族不飽和基との付加反応により硬化する付加反応型硬化性シリコン組成物が知られている。

【0003】しかし、縮合反応型硬化性シリコン組成※



【式中、R¹はアルケニル基を除く一価炭化水素基であり、R²はアルケニル基を除く一価炭化水素基または水

*【化1】

*

※物は、硬化時間が極めて長く、硬化性が悪いという問題があり、付加反応型硬化性シリコン組成物は、イオウ、ハンダフラックス等の付加反応阻害性物質の存在下では硬化が進行せず、また酸素により該組成物の表面が硬化しにくいという問題があった。また、一般に、硬化性シリコン組成物は、硬化後のシリコン硬化物の耐熱性が低いという問題があった。

【0004】このため、硬化性に優れた種々の硬化性シリコン組成物が提案されており、このような硬化性シリコン組成物として、エポキシ基含有有機シランの加水分解物と過塩素酸アンモニウムからなる硬化性シリコン組成物(特開昭56-72054号公報参照)、および1分子中に少なくとも2個のエポキシ基を含むオルガノポリシロキサンと1分子中に少なくとも2個のアミノ基を含むオルガノポリシロキサンとエポキシ硬化触媒とからなる硬化性シリコン組成物(特開昭60-178417号公報参照)が提案されている。

【0005】

【発明が解決しようとする課題】しかし、特開昭56-72054号公報および特開昭60-178417号公報により提案された硬化性シリコン組成物の硬化性は十分満足できるものではなく、また硬化後のシリコン硬化物の柔軟性および耐熱性が劣るという問題があった。

【0006】本発明者は、上記問題点を解決するため鋭意検討した結果、本発明に到達した。

【0007】すなわち、本発明の目的は、硬化性に優れ、硬化後は柔軟性および耐熱性に優れたシリコン硬化物となる硬化性シリコン組成物を提供することにある。

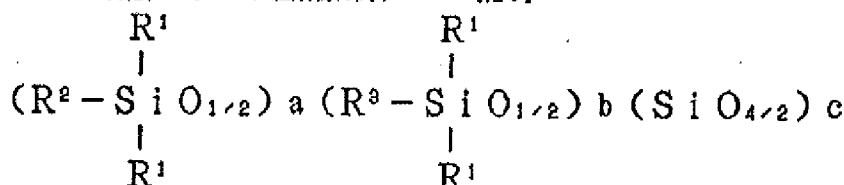
【0008】

【課題を解決する方法およびその作用】本発明は、(A)一般式：

【化2】

素原子であり、R³はエポキシ基含有有機基またはアルコキシシリルアルキル基であり、かつR³の内少なくとも

も1個はエポキシ基含有有機基である。また、aは0または正数であり、bは正数であり、cは正数であり、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。]で表されるオルガノポリシロキサン、および(B)硬化剤または硬化触媒からなる硬化性シリコン組成物に関する*



で表される。上式中、R¹はアルケニル基を除く一価炭化水素基であり、具体的には、メチル基、エチル基、プロピル基、ブチル基、ペンチル基等のアルキル基；フェニル基、トリル基、キシリル基等のアリール基；ベンジル基、フェネチル基等のアラールキル基；クロロメチル基、3, 3, 3-トリフルオロプロピル基等の置換アルキル基等が例示される。R²はアルケニル基を除く一価炭化水素基または水素原子であり、具体的には、水素原子またはメチル基、エチル基、プロピル基、ブチル基、ペンチル基等のアルキル基；フェニル基、トリル基、キシリル基等のアリール基；ベンジル基、フェネチル基等のアラールキル基；クロロメチル基、3, 3, 3-トリフルオロプロピル基等の置換アルキル基等が例示される。また、R³はエポキシ基含有有機基またはアルコキシシリルアルキル基であり、かつR³の内少なくとも1個はエポキシ基含有有機基である。エポキシ基含有有機基として、具体的には、グリシドキシエチル基、グリシドキシプロピル基、グリシドキシブチル基、3, 4-エポキシシクロヘキシルエチル基、3, 4-エポキシシクロヘキシルプロピル基、3, 4-エポキシノルボルネニルエチル基、2-(3, 4-エポキシ-3-メチルシクロヘキシル)-2-メチルエチル基等が例示され、また本発明の組成物に接着性を付与するためのアルコキシシリルアルキル基として、具体的には、トリメトキシシリルエチル基、トリメトキシシリルプロピル基、トリメトキシシリルブチル基、トリエトキシシリルエチル基、トリエトキシシリルプロピル基、トリプロポキシシリルエチル基※

する。

【0009】以下、本発明の硬化性シリコン組成物について詳細に説明する。

【0010】(A)成分のオルガノポリシロキサンは本発明の主材であり、一般式：

【化3】

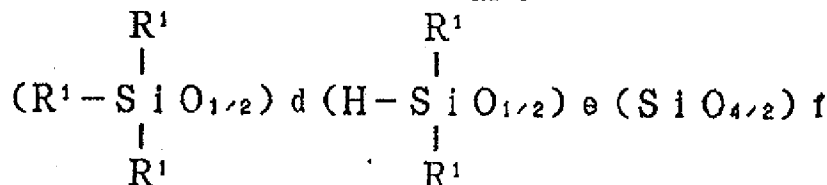
※ン、メチルジメトキシシリルエチル基、メチルジメトキシシリルプロピル基等が例示される。

【0011】また、上式中、aはエポキシ基含有有機基またはアルコキシシリルアルキル基を有しない一官能性シロキサン単位(M単位)の数を示す0または正数であり、bはエポキシ基含有有機基またはアルコキシシリルアルキル基を有する一官能性シロキサン単位(M単位)の数を示す正数であり、cは四官能性シロキサン単位(Q単位)の数を示す正数であり、それぞれの比、a/cは0~4の数であり、b/cは0.05~4の数であり、かつ(a+b)/cは0.2~4の数である。これは、四官能性シロキサン単位(Q単位)1個に対して、一官能性シロキサン単位(M単位)は4個をこえることはできず、また硬化後のシリコン硬化物が柔軟性および耐熱性に優れるためには、エポキシ基含有有機基もしくはアルコキシシリルアルキル基を有する一官能性シロキサン単位(M単位)は、四官能性シロキサン単位(Q単位)1個に対して少なくとも0.05個であることが必要であるからである。

【0012】(A)成分のオルガノポリシロキサンは室温で液状または固体状であり、その分子量は特に限定されないが、硬化性が優れることから、500~500,000の範囲であることが好ましい。

【0013】上記(A)成分のオルガノポリシロキサンは、例えば、ヒドロシリル化反応用触媒の存在下、一般式：

【化4】



{式中、R¹はアルケニル基を除く一価炭化水素基である。また、dは0または正数であり、eは正数であり、fは正数であり、d/fは0~4の数であり、e/fは0.05~4の数であり、かつ(d+e)/fは0.2~4の数である。}で表されるオルガノポリシロキサン

とエポキシ基含有脂肪族不飽和炭化水素と任意量のアルコキシシリルアルケンとを付加反応させることにより得ることができる。

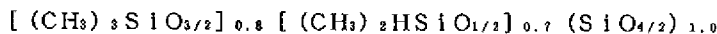
【0014】(B)成分の硬化剤または硬化触媒は、(A)成分のオルガノポリシロキサンを硬化させるための成分で

あり、(B)成分としては、一般にエポキシ樹脂を硬化させる硬化剤または硬化触媒であれば特に限定されない。硬化剤として、具体的には、フェノール化合物、カルボン酸化合物、酸無水物、アミン化合物、アルコキシ基含有化合物またはこれらの混合物や部分反応物が例示され、硬化触媒として、具体的には、イミダゾール等の3級アミン化合物、4級アミン化合物、ホスフィン等のリン化合物、有機アルミ等のアルミ化合物、有機ジルコニウム等のジルコニウム化合物等が例示される。また、本発明の組成物では、硬化剤または硬化触媒のいずれか一方または硬化剤と硬化触媒を併用して使用することができる。

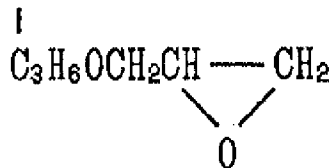
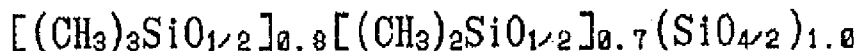
【0015】(B)成分の配合量は特に限定されないが、(A)成分100重量部に対して0.1~500重量部であることが好ましい。これは、(B)成分の配合量が(A)成分100重量部に対して0.1重量部未満では、硬化反応が起こり難くなるためであり、また500重量部を超えても硬化反応が十分に起こり難くなるためである。

【0016】また、本発明の硬化性シリコン組成物は、上記(A)成分と(B)成分からなるが、その他の成分として、煙霧状シリカ、結晶性シリカ、焼成シリカ、湿式シリカ、酸化チタン、炭酸亜鉛、炭酸カルシウム、酸化鉄、カーボンブラック等の充填剤、ステアリン酸エステル、パルミチン酸エステル等の高級脂肪酸エステルもしくは金属塩、エステル系ワックスまたは可塑剤等を配合することができる。

【0017】本発明の硬化性シリコン組成物は、硬化*

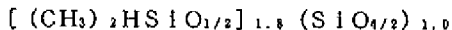


で表されるオルガノポリシロキサン（粘度105センチポイズ、ケイ素原子結合水素原子の含有量0.40重量%）をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオ※

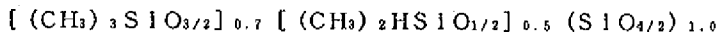


【0020】

【参考例2】式：



で表されるオルガノポリシロキサン（粘度46センチポイズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン(B)を得た。このオルガノポリシロキサンの粘度は610センチポイズであり、エポキシ当量は370であった。



*性に優れ、硬化後は柔軟性および耐熱性に優れたシリコン硬化物となるので、塗料、電子・電気部品のコーティング剤、接着剤、電気・電子部品用封止剤、自動車エンジン等の高温部周辺のシール剤さらには硬化性樹脂組成物の可撓性付与剤として好適に使用することができる。

【0018】

【実施例】以下、本発明を実施例により説明する。なお、実施例中、粘度の値は25℃において測定した値であり、硬化性シリコン組成物は、150℃で3時間加熱して硬化させた。また、シリコン硬化物の物理特性の測定は、以下のようにして行った。

○耐熱性：シリコン硬化物の小片を熱重量分析(TGA)により、空気下、昇温速度10℃/分で昇温し、850℃での残存率(重量%)で示した。

○柔軟性：1/4インチ×1/2インチ×4インチの棒状の成形したシリコン硬化物の両端を固定し、次いでシリコン硬化物の中心部に5kgの荷重をかけて、中心部の反りを測定した。その反りが0.5cm未満である場合を×とし、0.5~1cmである場合を△とし、1cmを超える場合を○として表した。

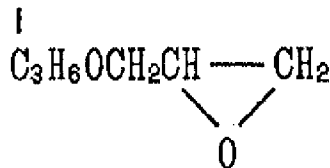
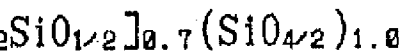
○硬度：2インチφ×1/10インチの円板に成形したシリコン硬化物を、バーコール935硬度計により測定した。

【0019】

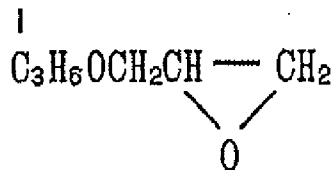
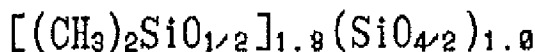
【参考例1】式：

※オルガノポリシロキサン(A)を得た。このオルガノポリシロキサンの粘度は520センチポイズであり、エポキシ当量は420であった。

【化5】



40 【化6】

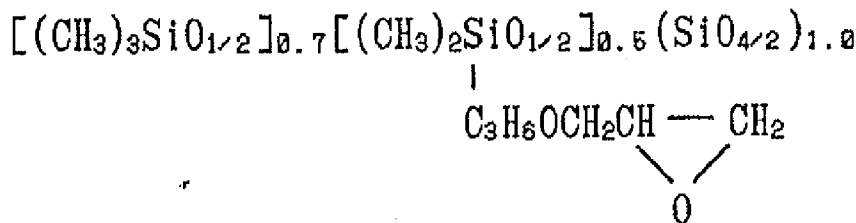


【0021】

【参考例3】式：

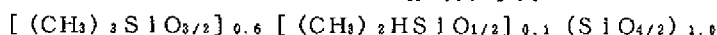
7

で表される粘稠なオルガノポリシロキサン（ケイ素原子結合水素原子の含有量0.33重量%）をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン*

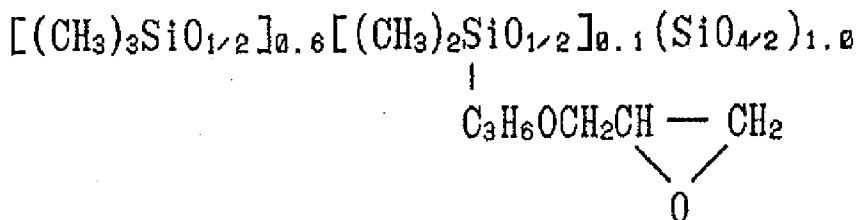


【0022】

※ ※【参考例4】式：

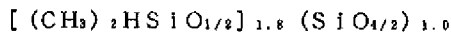


で表されるオルガノポリシロキサン（ケイ素原子結合水素原子の含有量0.09重量%）をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン★



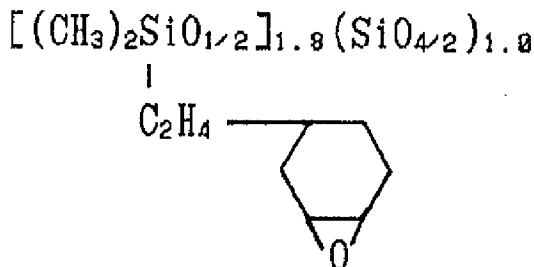
【0023】

【参考例5】式：



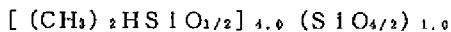
で表されるオルガノポリシロキサン（粘度46センチポイズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、過剰の1,2-エポキシ-4-ビニルシクロシロキサンを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン（E）を得た。このオルガノポリシロキサンは褐色透明であり、その粘度は520センチポイズであり、エポキシ当量は230であった。

【化9】



【0024】

【参考例6】式：



で表されるオルガノポリシロキサン（沸点190℃、ケイ素原子結合水素原子の含有量1.22重量%）をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金

8

*サン（C）を得た。このオルガノポリシロキサンは褐色半透明であり、エポキシ当量は1100であった。

【化7】

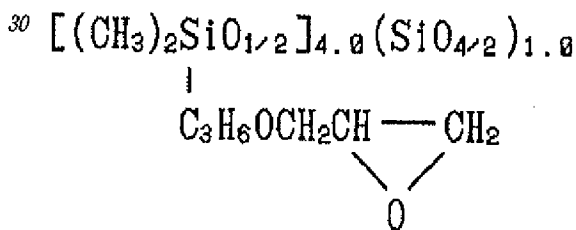
※ ※【参考例4】式：

★（D）を得た。このオルガノポリシロキサンは褐色透明であり、エポキシ当量は1290であった。

【化8】

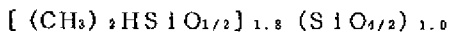
酸を触媒として反応させ、下式で示されるオルガノポリシロキサン（F）を得た。このオルガノポリシロキサンは褐色透明であり、その粘度は54センチポイズであり、エポキシ当量は205であった。

【化10】



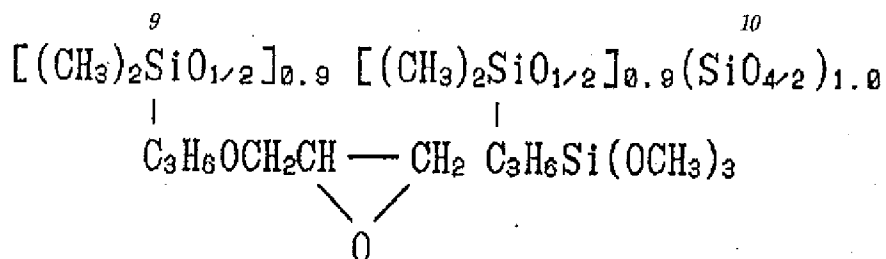
【0025】

【参考例7】式：



40 で表されるオルガノポリシロキサン（粘度46センチポイズ、ケイ素原子結合水素原子の含有量0.92重量%）をトルエン中で、オルガノポリシロキサン中のケイ素原子結合水素原子に対して、アリルグリシジルエーテルとアリルトリメトキシシラン=1:1からなる混合物を塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン（G）を得た。このオルガノポリシロキサンは黄色透明であり、その粘度は200センチポイズであった。

【化11】



【0026】

【実施例1】参考例で調製したオルガノポリシロキサン、3，4-エポキシシクロヘキシルメチル-3，4-エポキシシクロヘキサンカルボキシレート、3または4-メチルヘキサヒドロフタリックアンハイドライド、2，4，6-（トリスジメチルアミノメチル）フェノールを表1に示す重量部数で均一に混合して、硬化性シリコーン組成物を調製した。これらの硬化性シリコーン組成物を硬化させ、得られたシリコーン硬化物の物理特性を測定した。これらの結果を表1に示した。また、参考例2で調製したオルガノポリシロキサンBを配合してなる硬化性シリコーン組成物の硬化後の硬度は5.5であっ

た。

【0027】

【比較例1】また、比較のためオルガノポリシロキサンを除き、表1に示す重量部数で硬化性エポキシ樹脂組成物を調製した。この硬化性エポキシ樹脂組成物を実施例1と同様にして硬化させ、得られた硬化物の物理特性を測定した。この結果を表1に示した。また、この硬化物の硬度は5.5であり、実施例1において測定したシリコーン硬化物の硬度と差がないことが確認された。

【0028】

【表1】

	本 発 明						比較例
	A	B	C/F	D/G	E	F	
オルガノポリシリキサンの種類							—
オルガノポリシリキサン	100	100	95/5	95/5	100	50	—
3,4-エポキシシクロヘキシルメチル-8,4-エポキシシクロヘキサンカルボキシレート	—	—	—	—	—	50	100
3または4-メチルヘキサイト・D7タリツクアンライト・ライト	37.6	42.7	14.4	12.2	40.5	76.6	120.5
2,4,6-(トリシメチルアミノメチル)フェノール	1	1	1	1	1	1	1
柔軟性	○	○	○	△	△	△	×
残存率 (重量%)	33	25	55	63	27	11	0

【0029】

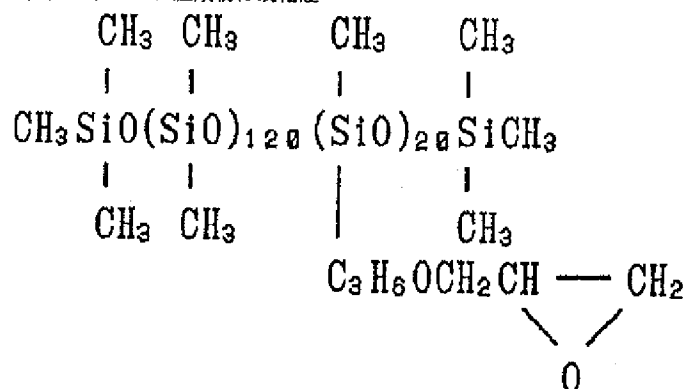
【実施例2】実施例1において、平均粒子径13 μ mの溶融シリカを添加した以外は実施例1と同様にして硬化性シリコン組成物を調製した。得られた硬化性シリコン組成物を実施例1と同様にして硬化させ、得られた

シリコン硬化物の物理特性を測定した。この結果を表2に示した。

【0030】

【表2】

【0031】
【比較例2】下式に示したオルガノポリシロキサンを使用した以外は実施例1と同様にして硬化性シリコーン組成物を調製した。この硬化性シリコーン組成物は硬化塗*
*上で下式のオルガノポリシロキサンが表面に分離したため硬化物の物理特性を評価することができなかった。
【化12】



【００３２】
【発明の効果】本発明の硬化性シリコン組成物は、
(Ａ)成分と(Ｂ)成分からなり、特に(Ａ)成分がエポキシ基 40
含有有機基を有する一官能性シロキサン単位（Ｍ単位）
と四官能性シロキサン単位（Ｑ単位）からなるオルガノ
ポリシロキサンであるので、硬化性に優れ、硬化後は柔
軟性および耐熱性に優れたシリコン硬化物となるとい
う特徴を有する。

【補正内容】

【0004】このため、硬化性に優れた種々の硬化性シリコーン組成物が提案されており、このような硬化性シリコーン組成物として、エポキシ基含有有機シランの加水分解物と過塩素酸アンモニウムからなる硬化性シリコーン組成物（特開昭56-72054号公報参照）、および1分子中に少なくとも2個のエポキシ基を含むオル

ガノポリシロキサンと1分子中に少なくとも2個のアミノ基を含むオルガノポリシロキサンとエポキシ硬化触媒とからなる硬化性シリコーン組成物(特開昭60-179417号公報参照)が提案されている。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0005

【補正方法】変更

*【補正内容】

【0005】

【発明が解決しようとする課題】しかし、特開昭56-72054号および特開昭60-179417号により提案された硬化性シリコーン組成物の硬化性は十分満足できるものではなく、また硬化後のシリコーン硬化物の柔軟性および耐熱性が劣るという問題があった。

*

【手続補正書】

【提出日】平成5年3月30日

【手続補正1】

【補正対象書類名】明細書

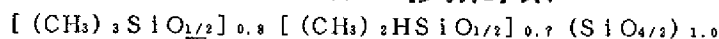
【補正対象項目名】0019

※【補正方法】変更

【補正内容】

【0019】

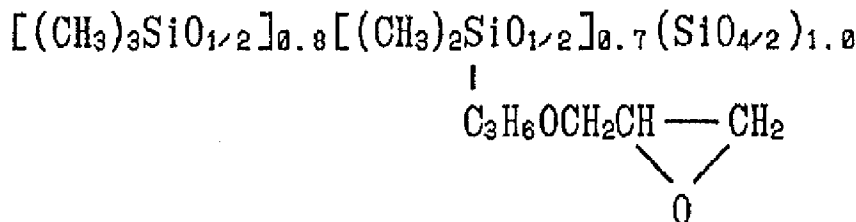
※【参考例1】式:



で表されるオルガノポリシロキサン(粘度105センチポイズ、ケイ素原子結合水素原子の含有量0.40重量%)をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキサン(A)を得た。このオルガノポリ★

★シロキサンの粘度は520センチポイズであり、エポキシ当量は420であった。

【化5】



【手続補正2】

【補正対象書類名】明細書

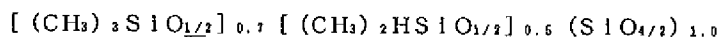
【補正対象項目名】0021

【補正方法】変更

☆【補正内容】

【0021】

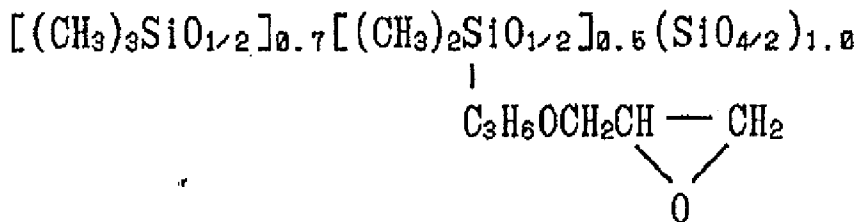
【参考例3】式:



で表される粘稠なオルガノポリシロキサン(ケイ素原子結合水素原子の含有量0.33重量%)をトルエン中で、過剰のアリルグリシジルエーテルを塩化白金酸を触媒として反応させ、下式で示されるオルガノポリシロキ◆

◆サン(C)を得た。このオルガノポリシロキサンは褐色半透明であり、エポキシ当量は1100であった。

【化7】



【手続補正3】

【補正対象書類名】明細書

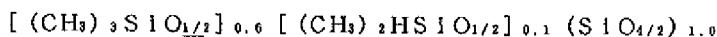
【補正対象項目名】0022

【補正方法】変更

*【補正内容】

【0022】

【参考例4】式:



で表されるオルガノポリシロキサン(ケイ素原子結合水

素原子の含有量0.09重量%)をトルエン中で、過剰

のアリルグリシルエーテルを塩化白金酸を触媒として
反応させ、下式で示されるオルガノポリシロキサン
(D)を得た。このオルガノポリシロキサンは褐色透明

であり、エポキシ当量は1290であった。
【化8】

